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DOI

[10.1016/j.fuel.2019.05.174](https://doi.org/10.1016/j.fuel.2019.05.174)

Publication date

2019

Document Version

Final published version

Published in

Fuel

Citation (APA)

Zhu, X., Zhao, L., Fu, F., Yang, Z., Li, F., Yuan, W., Zhou, M., Fang, W., Zhang, X., & More Authors (2019). Pyrolysis of pre-dried dewatered sewage sludge under different heating rates: Characteristics and kinetics study. *Fuel*, 255, Article 115591. <https://doi.org/10.1016/j.fuel.2019.05.174>

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Full Length Article

Pyrolysis of pre-dried dewatered sewage sludge under different heating rates: Characteristics and kinetics study

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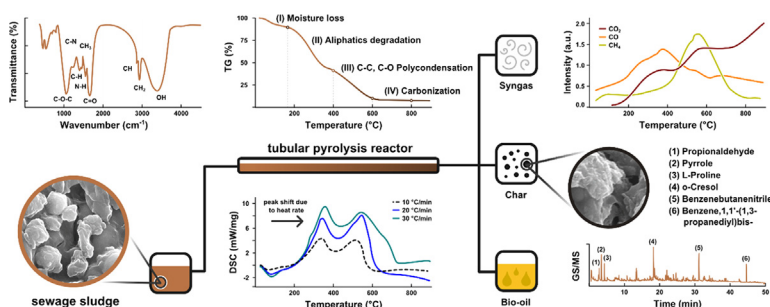
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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Pre-dried dewatered sewage sludge
Heating rate
TG-DSC-FTIR
Tubular reactor

ABSTRACT

The pyrolysis characteristics and kinetics of pre-dried dewatered sewage sludge under different heating rates (10, 20, and 30 °C/min) were investigated by thermogravimetric analyzer-fourier transform infrared analysis (TG-FTIR) and differential scanning calorimetry (DSC), and a heated tubular reactor. The thermal analysis results showed that four weight loss zones (< 165, 165–400, 400–600, and > 600 °C) were observed in TG curve, and a higher heating rate led to the increase of the maximum devolatilization rate and the higher temperature corresponding to the peak. The activation energy of different heating rate (10, 20, and 30 °C/min) was 70.0, 60.6 and 65.0 kJ/mol, respectively. The FTIR analysis of gaseous products indicated the concentrations of CO₂ and CO increased steadily with the increased heating rate, while the concentration of CH₄ first increased then decreased. Moreover, the yield of gaseous products and bio-oil increased with the increasing of the heating rate. Finally, the surface structure of chars and the chemical properties of bio-oil obtained were characterized using nitrogen adsorption, scanning electron microscopy, elemental analysis and gas chromatography–mass spectrometry. Overall, the results highlighted that pre-dried dewatered sewage sludge can be effectively converted into biofuel and porous material.

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1. Introduction

Sewage sludge is the main by-product of wastewater treatment process. It is produced in significant quantities during the process of rapid urbanization and industrialization in China, for example, over 3 Mt of dewatered sewage sludge (80% moisture content) was generated every each, most of which were not stabilized [1,2]. Meanwhile, the dewatered sewage sludge contains many different kinds of hazardous substances, which could lead to secondary environment pollution [3]. Thus, various treatment processes have been developed for sludge disposal, such as landfill, incineration and pyrolysis [4].

In recent years, landfill disposal is the main method of sludge treatment in China due to its higher capacity and lower investment. Biological treatment processes are considered the most environmentally and economically compatible of wastewater treatment methods [5]. Pre-dried dewatered sludge from a typical existing wastewater treatment plant (WWTP), situated in Shanghai, with about 60,000 m³/d capacity [6], was utilized as feedstock in this paper. Currently, the dewatered sludge from the A/A/O WTPP was discharged into Shanghai Laogang MSW Landfill after mechanical dewatering.

However, considering the requirements of stringent government legislation, the landfill and incineration technologies are becoming more and more difficult to operate [4,7]. Considering the opposition against the landfill or incineration, pyrolysis is a promising sludge disposal technology, which is more economical and environmentally friendly. As a new type of sludge disposal technology, pyrolysis has many advantages, such as volume reduction, accumulation of heavy metal, stabilization of waste [8]. Significant research has been carried out in sewage sludge pyrolysis, such as co-pyrolysis of microalgae and sewage sludge, fast microwave-assisted catalytic pyrolysis of sewage sludge, slow pyrolysis of sewage sludge [9–12]. Ridout et al. (2016) [12] studied both slow and fast pyrolysis processes for low and high ash paper sludge. They found fast pyrolysis yields higher production of condensable organic compounds and lower water compared with slow pyrolysis process. Dominguez et al. (2006) [13] compared microwave and conventional pyrolysis of two types of sewage sludge and the yield of syngas (H₂ + CO). The results indicate that microwave pyrolysis produced a higher proportion for syngas than conventional pyrolysis. Liu et al. (2015) [4] analyzed thermogravimetric and kinetic of dried industrial sludge pyrolysis, and found the kinetic study model can well describe the pyrolysis behavior and devolatilization mechanisms of the samples. The combustion and pyrolysis processes of dried sewage sludge were investigated by Thermogravimetric analysis (TGA) [14]. The results show the detailed identification of gaseous components evolved during the thermal reaction: mainly H₂, CO, CO₂ and CH₄. Moreover, the main devolatilization pyrolysis reactions was detected between 200 °C and 540 °C.

Based on the literature review that follows, the relative proportion and yields of the three pyrolysis products are mainly affected by process temperature, residence time of the feedstock and the raw materials' characteristics [15]. Sludge product yields generated from the pyrolysis process are determined by the raw material decomposition (primary) reactions and the intermediate reactions with the primary volatiles (secondary reactions) [16]. The high residence times and high temperatures limit mass transfer resulting in the facilitation of the secondary reactions [17]. Slow pyrolysis (SP) occurs under slow heating rates usually in the range of 1–60 °C min⁻¹ with long residence times (1 min to hours), when those of fast pyrolysis (FP) (300–12,000 °C min⁻¹) are shorter (< 2 s) [18]. TGA, which applies low heating rates (1–200 °C min⁻¹), can provide information on the composition of the material, order of reaction, number of different processes that take place in the reaction, and the corresponding kinetic constants [5]. Several kinetic models were proposed to describe the pathway of the formation of pyrolysis products and the related mechanisms of different kinds of waste biomass [1,16]. Meanwhile, a self-constructed special laboratory apparatus with retort is established in

this paper to explore the research of sludge pyrolysis. The retort-based apparatus can reduce errors caused by insufficiently homogeneous feedstock of TGA. Moreover, the retort apparatuses afford independent sampling of gaseous and liquid products for further analysis, as well as the direct determination of their mass, volume, physical properties and so on [11].

Regardless of the numerous studies on sewage sludge pyrolysis, only a few studies have based on a simultaneous application of both TG-FTIR and laboratory pyrolysis reactors to explore the influence of heating rates on the intermediate products and the structure of functional groups. Therefore, the aim of this study was to map the pyrolytic decomposition of pre-dried sewage sludge under the different heating rates, and to demonstrate the changes in amount and chemical composition, especially of bio-oil and pyrolysis gas. These values should be acclimated to the design and construction of an industrial system for the energetic and material use of dewatered sewage sludge.

2. Materials and methods

2.1. Materials

The sludge sample was collected from Quyang Municipal Wastewater Treatment Plant (WWTP) in Shanghai, China [6]. In order to analyze the chemical characteristics of sewage sludge, ultimate analysis and proximate analysis were carried out, and the results are shown in Table A.1. Before the pyrolysis, the sewage sludge was first dewatered by a vacuum pump (moisture content of 90%) and dried at 105 °C for 48 h (until a moisture content of 2%). Then, the pre-dried SS sample was ground by grinding mill and sieved through a 40 mesh and stored in seal PE bags until pyrolysis. The particle size of the pre-dried SS sample was less than 0.4 mm in this research.

2.2. FTIR analysis

The infrared spectrum of dried sewage sludge was examined by using VERTEX-70 Fourier transform infrared spectroscopy (FTIR) to analyze the organic functional groups. The samples were mixed with KBr powders at a mass ratio of 2:100 and pressurized into a pellet.

2.3. TG-DSC-FTIR analysis

The pyrolysis process of sewage sludge was analyzed by TGA (TG/DSC, STA 449 model, NETZSCH, USA) coupled with a Vertex70 spectrometer Fourier transform infrared spectrometer (FTIR) (Bruker, Germany). About 5 mg dried sludge was loaded in a crucible and heated in TG equipment with N₂ atmosphere at 10, 20, 30 °C min⁻¹ of heating rate from 30 °C to 900 °C. The N₂ flow rate was kept at 20 mL/min. The differential thermogravimetric (DTG) curves were collected by numerical derivation of the TG curves. The gaseous products from the pyrolysis of sewage sludge in TGA were determined using FTIR spectra. The transfer line and gas cell were heated at a temperature of 200 °C to avoid the condensation of volatile decomposition products. The wave number range of IR was 4000–600 cm⁻¹. The resolution and sensitivity were set at 4 cm⁻¹, and the spectrum scan frequency was 8 times per minute [19].

2.4. Pyrolysis experimental procedures

In this study, about 5–10 g dried sewage sludge was loaded in a quartz boat and heated in a horizontal tubular furnace reactor (see in Fig. A.1). N₂ was utilized as purging gas and the flow rate is 30 mL/s. The sewage sludge pyrolysis experiments under the different heating rates at 10, 20, 30 °C min⁻¹ of heating rate from 50 °C to 800 °C were investigated. Pyrolysis gases were collected by gas bags after a cooling unit. Wet gas meter was used to record the flow of the pyrolysis vapor during the pyrolysis experiments. The char and bio-oil was weighted

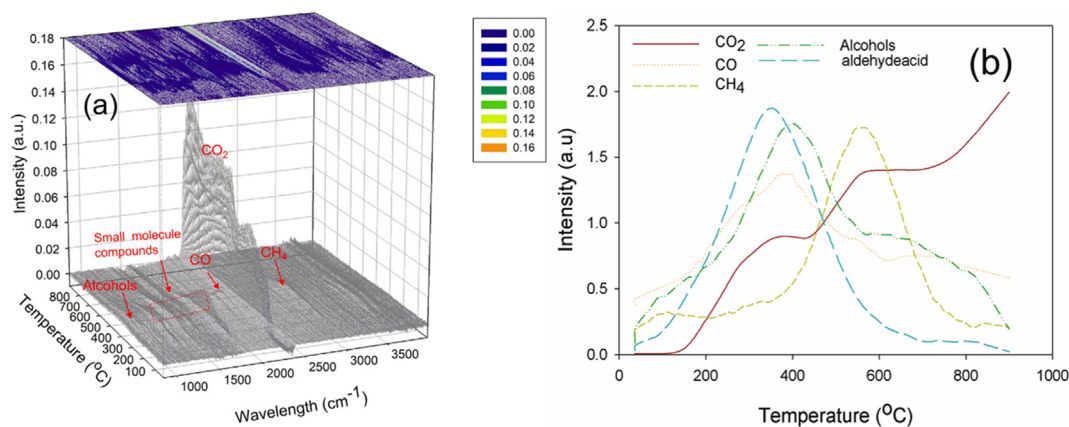


Fig. 1. (a) Three-dimensional TG-IR graph of sludge samples, and (b) product distribution from pyrolysis of sewage sludge.

after the complete cooling of the reactor. After that, the chars were analyzed by BET (ASAP 2020) and SEM/EDS (Hitachi, Japan). The pyrolysis gas (mainly about H₂, CO, CH₄, CO₂) was collected by the gas bag and analyzed off-line by gas chromatograph (GC) coupled with a thermal conductivity detector (TCD) [1].

2.5. Pyrolysis kinetics

The pyrolysis reaction of sludge can be described as follows [3]:

Sewage sludge → Residue + Volatile

The basic equations of dynamics can be described as,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where α is the sludge conversion at the time, T is reaction temperature, A is the pre-exponential factor (min⁻¹), E is apparent activation energy (kJ mol⁻¹), β is the heating rate, R is gas constant (8.314 J mol⁻¹ °C⁻¹), where α can be expressed as,

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty} \quad (2)$$

For the equation, W_t is the weight at any time, W_0 and W_∞ represent the initial and final weights of the sludge sample.

$f(\alpha)$ is presented as,

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

Combine Eqs. (1) and (2), the basic equation of dynamics can be given by,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (4)$$

In this study, the integral method (Coats and Redfern [1]) was used to calculate the activation energy of the non-isothermal degradation of sewage sludge. Eq. (4) can be integrated as follows,

$$\ln\left[-\frac{\ln(1 - \alpha)}{T^2}\right] = \ln\left[\frac{AR}{10E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (n=1) \quad (5)$$

$$\ln\left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)}\right] = \ln\left[\frac{AR}{10E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (n \neq 1) \quad (6)$$

As $\exp(-E/RT) \approx 0$, Eq. (5) and Eq. (6) can be simplified as

$$Y = \ln\left[-\frac{\ln(1 - \alpha)}{T^2}\right] \quad (n=1) \quad (7)$$

$$Y = \ln\left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)}\right] \quad (n \neq 1) \quad (8)$$

Thus $Y = kX + b$, $b = \ln\left[\frac{AR}{10E}\right]$, $k = -\frac{E}{R}$, $X = \frac{1}{T}$ and the apparent

activation energy E and the pre-exponential factor A , could be determined by the above method.

3. Results and discussions

3.1. FTIR spectra of sludge samples and pyrolysis products

In order to understand the pyrolysis characteristics of sludge, the distribution of function groups was detected by FTIR (see in Fig. A.2). It shows that there is a strong and broad absorption peak between 3300 and 3500 cm⁻¹, which represents molecular hydrogen bonds between the O-H stretching vibration. The absorption peak in the range of 1700–1750 cm⁻¹ is characterized by C=O stretching vibration, and 2820 cm⁻¹ absorption peak by aldehyde group C-H stretching vibration. C-C in 800–1250 cm⁻¹ within the scope of that feature is not strong. The absorption peak at 1460 cm⁻¹ represents C-H, 500–600 cm⁻¹ for C-I, and 550–850 cm⁻¹ for C-Cl. There is also a strong absorption peak between 1060 ~ 1150 cm⁻¹ induced by C-O-C stretching vibration [1,3,17,20].

The thermogravimetric analyzer is useful to study the mass-loss characteristics of samples at different heating rates under non-isothermal pyrolysis process. By coupling FTIR to TGA, the type and quantity of the gaseous products could be associated with the mass-loss characteristics during the pyrolysis [1,21].

Fig. 1 shows the three-dimensional FTIR spectra obtained from the gas volatilized and gaseous product distribution during the thermal decomposition of sewage sludge in a nitrogen atmosphere at a 20 °C/min heating rate. In Fig. 1a, the vertical axis is absorbance units, the horizontal axis is in wavenumbers, and the perspective axis represents the temperature. The pyrolysis gas was evolved between 100 °C and 700 °C. A typical spectrum demonstrated the characteristic wave numbers of gas species, including CH₄ (3025–3000 cm⁻¹), CO₂ (2400–2250 cm⁻¹), CO (2250–2200 cm⁻¹), and some organic volatile compounds such as small molecule lipid (1900–1200 cm⁻¹), aldehydes and acids (1820–1660 cm⁻¹), alcohols and phenols (980–950 cm⁻¹) [1,22].

As shown in Fig. 1b, the main gases were CO₂, CO, CH₄, and the alcohols and aldehyde acid were also observed. It can be seen that the production of CO₂ increased significantly with the rise of thermal decomposition temperature. The yield of CH₄ went up slightly at lower temperatures, and the intensity reached a maximum near the temperature of 600 °C. The production of CH₄ was reduced for higher pyrolysis temperatures. Many reports have pointed out that CH₄ is generated as a result of several reactions during pyrolysis [23].

3.2. TG DTG and DSC analysis

Fig. 2 shows the TG (wt%), DTG (wt%/°C) and DSC curves of the

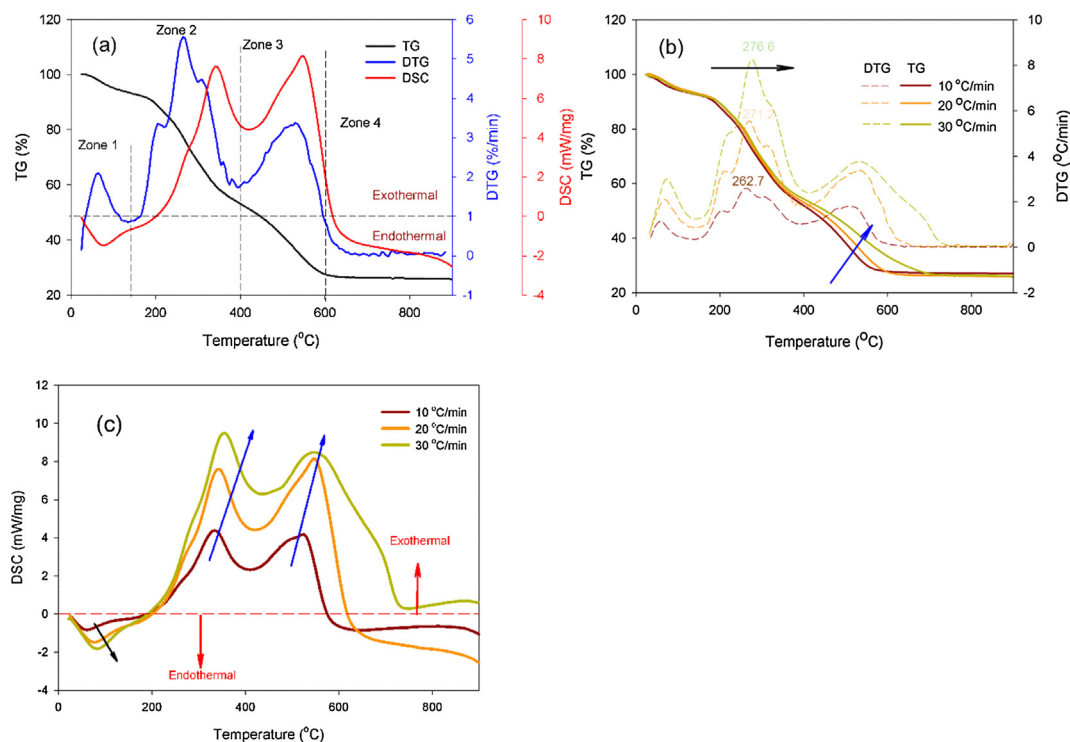


Fig. 2. (a) TG, DTG and DSC curves of sludge at 20 °C/min, (b) TG, DTG and (c) DSC curves of sludge at 10, 20 and 30 °C/min heating rate.

sludge during its heating from 20 to 900 °C at different heating rates.

As shown in Fig. 2a, the curves showed that the weight loss of the sludge had four zones (< 165, 165–400, 400–600, and > 600 °C), and the total weight loss rate was 74.29%. At the first zone, about 7.44 wt% of the total mass loss of initial sludge sample occurs, which is related to endothermic process resulting in the loss of moisture [20,24]. The second zone extended from 165 to 400 °C and was ascribed to the thermal degradation of medium molecular weight components in the sludge. It had the maximum rate of heat release (7.54 mW/mg). This stage is the main pyrolysis process, and about 39.00% of the total weight of sewage sludge weight was lost, containing residual moisture and easy to decompose organic compounds such as aliphatic compounds and lingo-cellulosic biomass [22,25,26]. During 400–600 °C, the small part of pyrolysis residue non-biodegradable organic matters such as lipid waxes and oils in sludge were decomposed [1,27], and the weight loss rate was 26.78%. From the DSC curve, the maximum exothermic peak was observed, and the maximum heat release rate is 8.16 mW/mg. Above 600 °C, the fourth stage which is related to the decomposition of inorganic materials shows much lower mass loss. The corresponding DSC curve shows a continued endothermic process. This might be due to the polycondensation of C–C bonds and C–O bonds that occurred in this temperature range [17,22].

Fig. 2b and c shows the variation of TG, DTG and DSC curves of sludge with the increase of heating rate. It was found that a higher heating rate led to an increase of the maximum devolatilization rate and the temperature corresponding to the peak. For example, the maximum degradation temperature was 262.7, 271.2 and 276.6 °C for the first step at heating rates of 10, 20 and 30 °C/min, with the corresponding the maximum mass loss rate of about 2.63, 5.57 and 8.27% min⁻¹, respectively. This shift of peak towards a higher temperature, with an increasing heating rate, might be caused by the effect of the kinetics of the decomposition, which resulted in a delayed degradation. This observation was consistent with that of [28] who reported that a higher heating rate resulted in a sharper peak of DTG curves and a higher temperature for its occurrence. From Fig. 2b, the maximum final agravic quotient of the sludge pyrolysis is at the heating

rate of 10 °C/min, indicating that the final agravic quotient of sludge was affected by different heating rates, while the excessive heating rate would delay the process of the sludge pyrolysis as the volatile components within sludge were unable to release immediately. The residual water content in sludge deposited at the first loss mass peak that ended at the temperature of 140 °C. At the second loss mass peak, most substances in the pyrolysate are aliphatic compounds and protein. At the same time, the maximum precipitation rate of the volatile compounds is at the temperature range of 140–400 °C. And the last mass loss peak was observed between 400 and 600 °C, which consists of carbohydrate compounds. With the increase of heating rate, the exothermic peak became larger even at the same temperature, which can be seen from DSC curves (Fig. 2c). For sludge, three obvious exothermic peaks were found in the DTG curves at the temperature of 350, 540 and 700 °C.

From the TG and DTG curves in Fig. 2b, it could be observed the sludge samples have the same variation trend under different heating rates, indicating that the heating rates had little effect on the pyrolysis of sludge under the pyrolysis conditions in this work. In general, the decomposition rate of sewage sludge increased with the increase of heating rate. In each stage, the starting temperature, final temperature and temperature of maximum reaction rate increased to different degrees with the increase in heating rate, while the main reaction region decreased. Furthermore, the initial pyrolysis stage increased, and the DTG curve moved to higher temperatures with the increase in the heating rate.

In addition, the total mass loss for sludge at the three different heating rates changed slightly, which is in the range of 73–76%. For the heating rate of 30 °C/min, the total mass loss is 71.90%, which is less than that at 10 °C/min, which is 72.91%, indicating that the quick heating delayed the pyrolysis reaction because the medium diffusion and heat transmission need some time. As a result, the total mass loss increased at a lower heating rate of 10 °C/min, while the external heat supply reduced accordingly, and the carbonization reaction aggravated as the pyrolysis time extended, and the amount of volatile matter decreased [17]. At the same time, moisture weight loss, ash weight loss and volatiles weight loss of sludge sample obtained by TG experiment

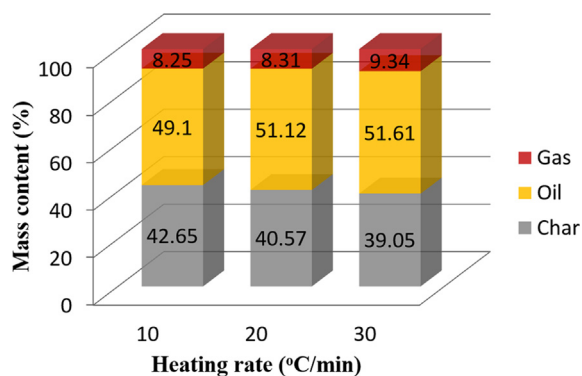


Fig. 3. Products distribution of sewage sludge pyrolysis for different heating rates.

were true to sludge proximate analysis data which showed that the thermal analysis experiments were reasonable.

3.3. Kinetic analysis

The activation energy and pre-exponential factors of non-isothermal analysis of sewage sludge pyrolysis by TGA are presented in Table A.2. High correlation coefficients indicated that the first order reaction model fits the experimental data very well. The fitting equations are shown in Table A.2. The activation energy and frequency factor at the heating rate of 10 °C/min were 70.0 kJ mol⁻¹ and 0.036 s⁻¹, respectively. While at the heating rate of 20 and 30 °C/min, the values of activation energy and frequency factor were 60.6 kJ mol⁻¹, 65.0 kJ mol⁻¹ and 0.046 s⁻¹, 0.043 s⁻¹, respectively, indicating that the variation trend of activation energy is not obvious with the increasing of the heating rate during the sludge.

3.4. Products distribution of dried sewage sludge pyrolysis

Fig. 3 Shows the products distribution of sewage sludge pyrolysis for different heating rates. It was found that with the increasing heating rates, the tar yields and the gas yields showed a little fluctuation trend in the range of 49.1–51.61% and 8.25–9.34%. This might be the result of the condensation of vapor into tar before the organic bonds were broken. The char yields showed an inverse trend, which decreased from 42.65% at 10 °C/min to 39.05% at 30 °C/min. In general, the ratio of oil and gas yields are the largest in the heating rate of 30 °C/min, and the heat absorption of the sludge increased with the rise of heating rate as the molecular bond of the sludge cracked. This is consistent with the results of Kan, who indicated that increasing the heating rate resulted in an increase in the total gas yield [17].

The product gases of sludge pyrolysis included CO₂, CO, CH₄, and H₂. The compositions of gases produced under different heating rates are shown in Table 1. It shows that the concentrations of CO₂ increased steadily with the increase in heating rate from 10 to 30 °C/min. A possible reason for these results was the gasification of water in the sludge into vapor under higher temperature. In the case of carbon residue, CO₂ and CH₄ might result from the following reaction:



Table 1

Gas composition for different heating rates.

| Heating rate (°C/min) | CO ₂ (mmol/g) | CO (mmol/g) | CH ₄ (mmol/g) | H ₂ (mmol/g) | Gas produced per unit of sludge (kg/kg) | Calorific value of gas (MJ/kg) |
|-----------------------|--------------------------|-------------|--------------------------|-------------------------|---|--------------------------------|
| 10 | 1.5 | 0.36 | 0.337 | 0.548 | 0.0825 | 7.13 |
| 20 | 1.53 | 0.343 | 0.31 | 0.583 | 0.0831 | 6.84 |
| 30 | 1.74 | 0.375 | 0.323 | 0.574 | 0.0935 | 6.28 |



In the case of higher heating rate, the vapor reacted with char, while CH₄ and C were transformed into CO₂. From Table 1, it can be observed that the gas production quantity per unit of sludge was the highest and the calorific value of gas was the lowest at the heating rate of 30 °C/min. Therefore, from the view of energy utilization, it is more suitable to set the heating rate at 10 and 20 °C/min. After full reaction at high temperature, the sludge got more H₂ and CO, and the pre-generated CH₄ and CO₂ are more involved in the high temperature reforming reaction. Some researchers reported that the yield of hydrogen increases with the rise in temperature, due to the fact that the higher temperature facilitates the efficiency of gasification reactions, promoting the destruction of tar effectively promoting further gas yield [29]. However, Table 1 shows that the higher heating rate had little effect on gas production in the low-temperature zone.

According to the research from [30], the reaction time could be shortened in a low-temperature region of sludge by increasing the heating rate, and a large amount of organic matter produced in the high-temperature zone (350–550 °C) could improve the cumulative gas release amount. From the experimental results and theoretical analysis, it is found that the increase of the heating rate had a certain promotion effect, but not as much as the final temperature did for the gas production quantity.

SEM images showed that the morphology of dried sludge and chars in Fig. 4. It could be detected bio-char generate the porous structure after pyrolysis compared with the dried sludge. Meanwhile, due to the BET analysis, we found that the pyrolysis increased the surface area of dried sludge (2.47 m²/g) to char (9.42 ± 2.67 m²/g). Moreover, it can be observed from Table 2, the ultimate analysis showed that the char particles produced relatively higher C/H ratio. The BET surface analysis results accord well with those from other studies conducted on char at low heating rates [31,32].

Fig. 5 shows the GC/MS of the bio-oil from pyrolysis of sludge under the heating rate of 20 °C/min. There are approximately 8 main peaks, which represents typical organic components of the liquid fraction obtained from the pyrolysis of sludge [33–35]. L-Proline (RT = 4.85 min), and o-Cresol (RT = 18.42 min), Benzene butane nitrile (RT = 31.72 min) and Benzene (RT = 44.76 min) were the most abundant components in the bio-oils. The peak at the retention time of 2.04 min is Propionaldehyde. The peaks at the retention time of 2.04, 4.24, 13.29, 21.53 min represent Propionaldehyde, Pyrrole, 1-ethyl-3-methyl-Benzene and ketone, respectively. A significant amount of bio-fuel compound, namely alkanes/cycloalkanes, alkenes, and aromatics was present in bio-oil. Similar results are observed in other paper [35]. However, for transportation application fuel, the presence of phenol compounds and nitrogen-containing compounds must be removed due to the lowering heating value and NO_x emissions [35]. As the GC/MS analyses had already indicated, it was possible to detect several other compounds at sufficiently high concentration to enable the acquisition of elucidative mass spectra. This work shows that GC/MS can be a useful tool to indicate the presence of complex compounds by detection of its pyrolysis product [17,36].

4. Conclusions

The present work verified the successful application of combining of TG-DSC-FTIR and pyrolysis reactor to illuminate slow pyrolysis

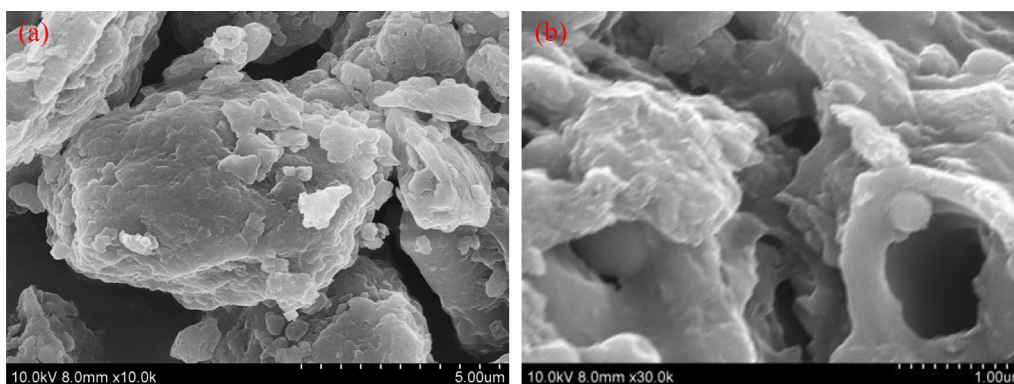


Fig. 4. SEM of sludge (a) and char (b) produced by pyrolysis.

Table 2

Ultimate analysis of sludge and char.

| Ultimate analysis (%) | C | H | N | S | C/N | C/H |
|-----------------------|--------------|-------------|-------------|-------------|-------------|--------------|
| Sludge | 36.33 | 5.44 | 6.49 | 0.87 | 5.59 | 6.68 |
| Char | 28.39 ± 2.67 | 1.27 ± 0.44 | 3.82 ± 0.79 | 0.31 ± 0.12 | 7.43 ± 1.34 | 22.31 ± 3.52 |

n = 3, the average and standard deviations of the parameters were calculated from the data of three different heating rates.

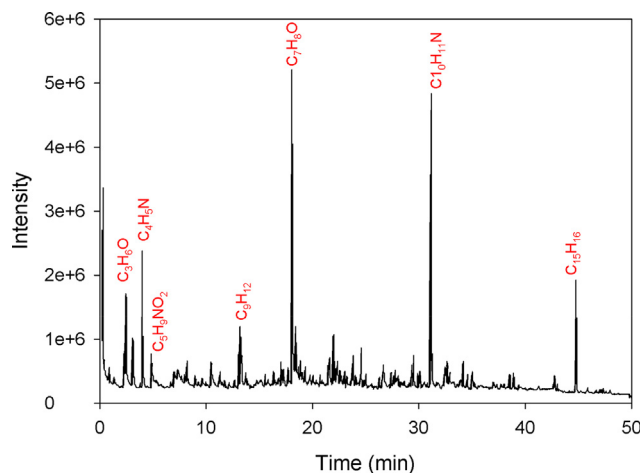


Fig. 5. GC-MS chromatogram of the product oil from pyrolysis of sludge at heating rate of 20 °C/min (the data of 10, and 30 °C/min is not shown here as there are no significant difference among the GC-MS data of the different heating rates).

characteristics and kinetics of pre-dried sewage sludge. The thermal analysis showed that the main decomposition zone of sample was in the range of 140–600 °C and the mass loss was 74.29% of the total sludge mass. Increasing heating rate from 10 to 30 °C/min resulted in the shift of the mass loss rate and endothermal/exothermal peaks to higher temperatures. The main gaseous components in the pyrolysis process were methane, carbon dioxide, carbon monoxide. Moreover, the higher heating rates improved the yield of gaseous products and bio-oil. Meanwhile, higher BET surface area and higher C/H ratio of porous bio-char was observed after tubular pyrolysis treatment. GC/MS results of the bio-oil indicated it contains not only a great amount of biofuel compound (alkanes/cycloalkanes, alkenes, and aromatics), but also abundant phenol and nitrogen-containing compounds. It was also found that no clear tendency may be established of the evolution of the activation energy and functional groups in the pyrolysis products with the increase of heating rate.

Acknowledgements

This work was sponsored by the National Natural Science Foundation of China (Nos. 21507079, 51808226, 21876106), the Science & Technology Innovation Action Plan of Shanghai under the Belt and Road Initiative (No. 17230741100), the Distinguished Professor in Universities of Shanghai (Oriental Scholar, No. TP2017041), the Shanghai Pujiang Program (No. 17PJ1402100), the Fundamental Research Funds for the Central Universities (Nos. 40500-20101-222001, 40500-20101-222078, 13903-120215-10435), and Gaoyuan Discipline of Shanghai-Environmental Science and Engineering (Resource Recycling Science and Engineering).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2019.05.174>.

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